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Bias-plasma assisted RF magnetron sputter deposition of hydrogen-less amorphous silicon

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Abstract

The execution of special hydrogen diffusion experiments requires an initially hydrogen-free drain layer. Hydrogen-free amorphous silicon (a-Si) deposited by radio frequency magnetron sputter deposition (RFSD) serves this purpose. RFSD yields a rough surface of the film but this can be flattened by an additional post-hydrogenation step. Weak Si-Si bonds are reorganized by hydrogen and the surface becomes smoother. However, by post-hydrogenation the a-Si layer loses its hydrogen-free characteristic. Bias-plasma assisted RFSD offers the possibility of a direct deposition of hydrogen-free a-Si films that exhibit a smooth surface. In this way an amorphous network with only few vacancies and related defects can be achieved as a consequence of the reorganization of weak Si-Si bonds during bias-plasma assisted deposition. Using a crystalline silicon wafer as base substrate for deposition the bias-plasma can additionally be used to prepare the c-Si surface whereby the HF-dip for removing native oxide can be omitted. The optimal deposition temperature of RFSD without bias-plasma, with respect to surface passivation, is ~325°C. Bias-plasma assisted RFSD leads to an additional interaction of atoms on the surface of the growing a-Si layer with atoms in the bias-plasma. This interaction decreases the optimal deposition temperature to ~275°C. Furthermore, the bias-plasma related flattening of the a-Si surface yields higher passivation quality of post-hydrogenated thin layers (≤ 40 nm) while the formation of additional ion induced defects decreases the passivation quality of thick (>> 40 nm) a-Si layers.

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1. Introduction

Radio frequency magnetron sputter deposition (RFSD) offers the possibility to deposit hydrogen-free amorphous silicon (a-Si) on crystalline silicon (c-Si). The RFSD technology uses a solid target consisting solely of the material intended to be deposited whereby deposition of hydrogen-free a-Si becomes possible [1].

Hydrogen-less a-Si layers could be used as a drain layer for advanced hydrogen diffusion experiments [2]. Furthermore, analyzing formerly hydrogen-less a-Si during a post-hydrogenation step allows determining hydrogen related influences on electrical, optical and structural characteristics [3]. As discussed in Ref. [3], the investigation of the progress of hydrogen based saturation of defects like dangling bonds and the related reduction of surface recombination velocity with post-hydrogenation duration can be evaluated by effective minority carrier lifetime measurements (τ_{eff}).

Compared to parallel-plate plasma-enhanced chemical vapor deposition (PECVD) there is not a direct plasma contact of the sample in the RFSD reactor whereby a plasma induced reorganization of weak Si-Si bonds during deposition is missing. Therefore a higher optimal deposition temperature with respect to surface passivation is needed. While several publications have shown that an optimal deposition temperature of PECV-deposition is at ~250°C, the optimal deposition temperature of RFS-deposited a-Si is ~325°C [3-7].

Bias-plasma assisted RFSD (BPA-RFSD) uses a second plasma directly above the sample leading to a smooth surface of the a-Si layer. This effect is probably based on the mentioned plasma induced reorganization of weak Si-Si bonds. This paper points out the advantages of the bias-plasma induced reorganization of weak Si-Si bonds already during deposition. Changes in the structural characteristics of deposited films will also be investigated as changes in the electrical characteristic after a post-hydrogenation step.

An application for BPA-RFS-deposition is the preparation of hydrogen drain layers for hydrogen diffusion and effusion experiments. As discussed in Ref. [3] for such experiments it is desirable to work with hydrogen-less amorphous layers with a very smooth surface to reduce misinterpretations at the (i) a-Si surface while measuring and analyzing hydrogen depth profiles.

2. Sample preparation and experimental conditions

The here investigated intrinsic (i) a-Si layers are RFS-deposited at a pressure of 2 mTorr using only Ar as process gas. Bias-plasma assisted as well as standard RFS-deposition takes place in an "AJA ATC 2200" RF magnetron sputtering system. For the experiments phosphorous doped (n-type) chemically polished float-zone (FZ) silicon wafers (c-Si) are used (5 Ωcm, 250 µm <100> oriented). If necessary, native oxide at the surface of the c-Si wafers is chemically removed in diluted hydrogen fluoride solution (HF) directly before RFS-deposition [3].

Surface roughness of RFS-deposited (i) a-Si layers are analyzed by atomic force microscopy (AFM) [8]. AFM analyses are carried out using an "Asylum Research MFP-3D" in non-contact mode by scanning an (1 × 1) µm^2 area with 2^{16} points (256 × 256).

Several samples are deposited with or without bias-plasma by varying layer thickness as well as deposition temperature. The samples are post-hydrogenated using a MIRHP (microwave-induced remote hydrogen plasma) reactor at a temperature of 370°C [9]. According to Ref. [3] the duration of the post-hydrogenation step depends on the thickness of the amorphous layer. All here investigated layers are post-hydrogenated for 100 min/nm [3]. During post-hydrogenation hydrogen accumulates in the RFSD (i) a-Si, saturates defects like dangling bonds and yields finally surface passivation of the c-Si. Comparing τ_{eff} of post-hydrogenated (i) a-Si (standard and bias-plasma assisted RFSD) allows investigating the influence of bias-plasma during the deposition process. The values of τ_{eff} itself are measured by transient and quasi-steady-state photo conductance decay at ~25°C (WCT 120, Sinton Instruments) [10].

3. Surface roughness

The topography of hydrogen-less RFS-deposited a-Si becomes highly uneven while the surface roughness is also high (Fig. 1, a) [3]. The statistical evaluation of the standard deviation of surface roughness (R_q) (Ref. [11]) is shown

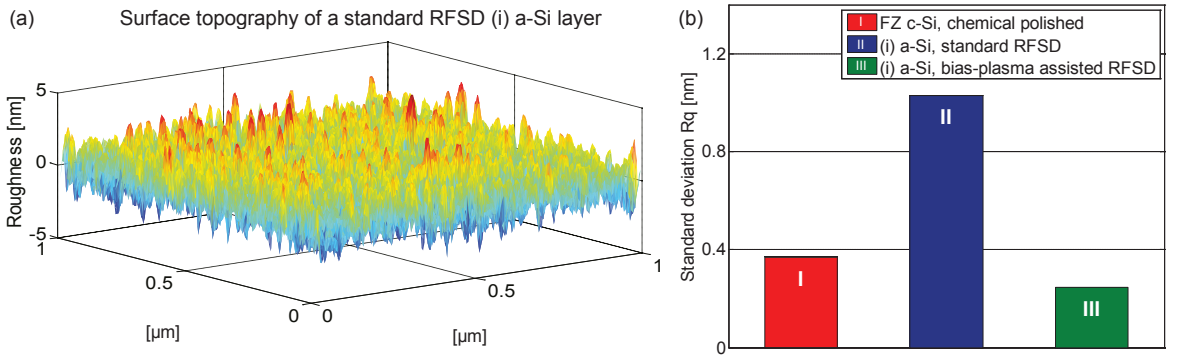

Fig. 1. (a) AFM measured surface topography of a 115 nm thick standard RFSD-deposited (i) a-Si layer; (b) comparison of the standard deviation of the surface roughness calculated from surface topography.

in Fig. 1 (b). In more detail, the bar graph compares R_q of a standard RFS-deposited (i) a-Si layer and a bias-plasma assisted RFS-deposited (i) a-Si layer with a chemical etched FZ c-Si wafer.

The bar graph in Fig. 1 (b) shows that, R_q of a standard RFSD (i) a-Si layer is ~1 nm. It can be assumed that due to the missing direct plasma contact the surface of the (i) a-Si becomes rougher during standard RFS-deposition compared to BPA-RFSD.

The roughness, calculated (Fig. 1, b) from the AFM measured surface topography (Fig. 1, a), is higher than for the chemical polished FZ c-Si reference material (R_q = 0.4 nm).

As shown in Fig. 1 (b) the standard deviation of a BPA-RFS-deposited (i) a-Si layer is about 0.25 nm and even lower than for the chemical polished FZ c-Si reference. BPA-RFSD provides direct contact of the growing (i) a-Si surface with a plasma leading to a smooth surface. It can be supposed that the smoothening of the surface occur by breaking up weak Si-Si bonds as well as disintegrating Si structures sticking out of the surface.

As mentioned in Ref. [3] the surface roughness of standard deposited RFSD (i) a-Si becomes lower during an additional post-hydrogenation step using remote hydrogen plasma and a reduction of R_q of ~20% is achieved (~1 nm → ~0.8 nm). Whereas this is a significant reduction of the surface roughness, R_q of an BPA-RFS-deposited (i) a-Si layer this is still lower.

4. Plasma induced surface preparation

The abrasive process of BPA-RFS-deposition smoothening the surface of the growing (i) a-Si layer can be used for surface preparation prior to deposition. The HF-dip for removing native oxide can be omitted if the bias-plasma is ignited prior to the main-plasma. During this first period of the process the bias-plasma sputters the surface of the c-Si sample and removes the native oxide.

As can be seen in Fig. 2 (a, ♦) the combination of BPA-RFSD and HF-dip yields a low surface passivation quality of post-hydrogenated samples ($\leq$ 50 µs) indicating a high concentration of defects at the (i) a-Si/c-Si interface. These interface defects are a consequence of the mentioned abrasive effect of the bias-plasma [3]. Therefore, there is an optimum time period between ignition of the bias-plasma to remove the native oxide and the ignition of the main-plasma to cover the c-Si with (i) a-Si and to "protect" the surface of the c-Si sample. The here discussed samples are deposited including a bias-plasma cleaning step of ten seconds.

5. Deposition conditions

5.1. Deposition temperature

As discussed in section 4, the smoothening of the surface during BPA-RFSD can be attributed to a continuous plasma related reorganization of weak Si-Si bonds. Furthermore, in consequence of the ongoing reorganization process a decrease of defects in the (i) a-Si layer can be supposed.

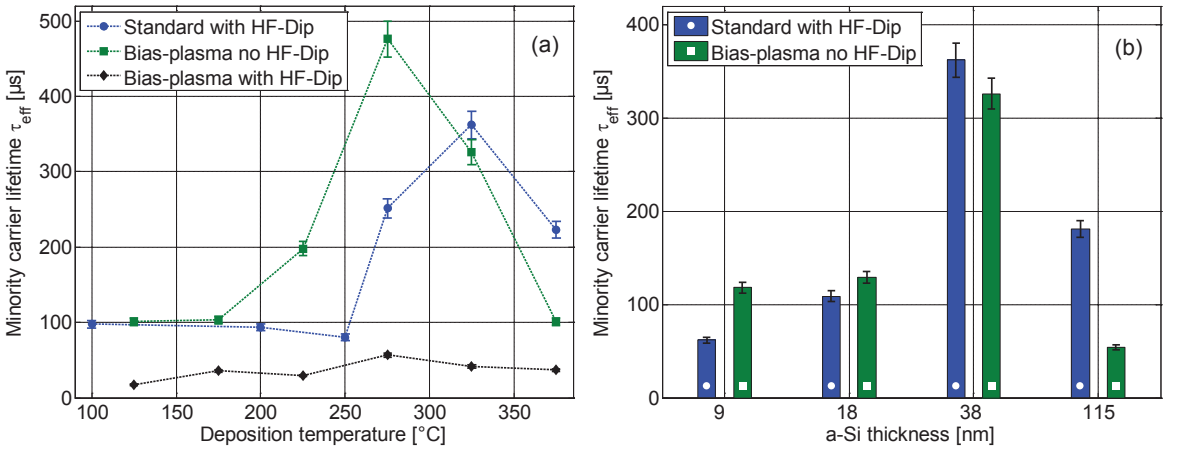

Fig. 2. (a) Minority carrier lifetime (τ_{eff}) of ~40 nm thin (i) a-Si layers RFS-deposited with and without bias-plasma assistance as a function of RFSD temperature as well as comparison of bias-plasma assisted RFSD with and without an additional HF-dip; (b) τ_{eff} of (i) a-Si layers RFS-deposited with varying thicknesses with and without bias-plasma enhancement.

Fig. 2 (a) shows i. a. the evolution of τ_{eff} after the mentioned post-hydrogenation step of (i) a-Si layers, RFS-deposited with (■) and without (●) bias-plasma assistance and as a function of RFS-deposition temperature. The post-hydrogenation itself occur using a hydrogen remote plasma at a temperature of 370°C for a duration of 100 min/nm [3].

The maximum of τ_{eff} for RFSD (●) is ~360 µs while surface passivation quality of BPA-RFS-deposited and post-hydrogenated (i) a-Si rises up to ~480 µs.

With respect to surface passivation several publications have shown that an optimal deposition temperature for a-Si deposited on c-Si wafers by using a direct-plasma reactor like PECVD is~250°C [4-6]. Moreover, several published investigations of RFSD a-Si layers (direct- as well as post-hydrogenated ones) mention an optimal RFS-deposition temperature of ~325°C [3, 7]. The missing interaction of atoms on the surface of the growing a-Si layer with atoms in the plasma seems to drive the optimal process to higher deposition temperatures.

As can be seen in Fig. 2 (a) the optimal deposition temperature, with respect to surface passivation, decreases from 325°C (●) to ~275°C (■) when using BPA-RFSD.

This is slightly higher than the optimal temperature of PECV-deposition of 225°C…250°C [4, 5]. Furthermore these findings support the conclusion of Ref. [3] mentioning that the higher deposition temperature of the RFS-deposition is related to the missing direct plasma contact.

5.2. Layer thickness

Fig. 2 (b) shows the evolution of τ_{eff} for RFSD (i) a-Si layers (deposited at 325°C) with varying thicknesses deposited with (■) and without (●) bias-plasma assistance. As mentioned in literature [3, 7], the optimal layer thickness of RFSD (i) a-Si with respect to the passivation quality is ~40 nm. As can be seen in Fig. 2 (b) the here investigated RFSD as well as BPA-RFSD (i) a-Si layers shows the same behavior and exhibit an optimal layer thickness of ~40 nm. The absolute value of τ_{eff} of BPA-RFSD (■) is lower compared to ● because Fig. 2 (b) compares layers deposited at 325°C.

Furthermore, it can be seen in Fig. 2 (b), that the surface passivation quality of BPA-RFS-deposited thin (i) a-Si layers (■) increases (< 40 nm), compared to RFSD layers (●) of the same thickness. In more detail, τ_{eff} of a ~9 nm thin (i) a-Si layer deposited by RFSD is nearly half of the value of a BPA-RFSD (i) a-Si layer of the same thickness (RFSD: $\tau_{eff} \approx 62$ µs; BPA-RFSD: $\tau_{eff} \approx 118$ µs) whereas τ_{eff} of ~18 nm RFSD (i) a-Si is only ~15% lower than BPA-RFSD (i) a-Si (RFSD: $\tau_{eff} \approx 109$ µs; BPA-RFSD: $\tau_{eff} \approx 129$ µs).

The sputter process itself causes damage to the a-Si bulk as well as to the a-Si/c-Si interface and the c-Si by a high energy photon-induced formation of defects [12]. Using an additional bias-plasma direct in front of the sample

increases the formation of such defects. Due to this, the surface passivation quality of thick BPA-RFS-deposited (i) a-Si layers (▬) decreases significantly compared to RFS-deposited (i) a-Si layers (▬).

6. Conclusions

A bias-plasma assisted RFS-deposition of hydrogen-less (i) a-Si yields several benefits compared to "standard" RFS-deposited layers.

- Smoothening the surface,
- Plasma induced surface conditioning, HF-dip can be omitted,
- Lowering of the optimal deposition temperature (325°C → 275°C),
- Surface passivation quality of thin layers (≤ 40 nm) increases (additional post-hydrogenation necessary).

Beside these positive issues one negative aspect has to be mentioned. Due to the additional bias-plasma the formation of ion (as well as radical) induced defects increases. This leads to a significant decrease of passivation quality for thick (>> 40 nm) BPA-RFSD (i) a-Si layers compared to RFS-deposited ones.

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References

[1] Tanaka K, Maruyama E, Schimada T, Okamoto H. Amorphous silicon. John Wiley & Sons. Chichester; 1999.
[2] Choi SY. Methods for forming a hydrogen free silicon containing dielectric film. Patent WO 2012024114, 19.07.2012.
[3] Gerke S, Becker H-W, Rogalla D, Singer F, Brinkmann N, Fritz S, Hammud A, Keller P, Skorka D, Sommer D, Weiß C, Flege S, Hahn G, Job R, Terheiden B. Influence of post-hydrogenation upon electrical, optical and structural properties of hydrogen-less sputter deposited amorphous silicon. Submitted to Thin Solid Films (TSF-S-15-00827), April 2015.
[4] Dauwe S, Schmidt J, Hezel R. Very low surface recombination velocities on p- and n-type silicon wafers passivated with hydrogenated amorphous silicon films. In: Proc 29th IEEE PVSC, New Orleans 2002. p. 1246-9.
[5] Knights JC, Lucovsky G. Hydrogen in amorphous semiconductors. CRC Cr Rev Sol State 1980;9:211-83.
[6] Street RA, Cahn RW, Davis EA, Ward IM. Hydrogenated amorphous silicon. Cambridge University Press. Cambridge; 1991.
[7] Zhang X, Hargeaves S, Wan Y, Cuevas A. Surface passivation of crystalline silicon by sputter deposited hydrogenated amorphous silicon. Phys Status Solidi RRL 2014;8:231-4.
[8] Binning G, Quate CFGC. Atomic Force Microscope. Phys Rev Lett 1986;56:930-3.
[9] Gloger S, Brinkmann N, Terheiden B. Low surface recombination velocity using amorphous silicon on industrial-type cleaned surfaces. En Proc 2011;8:666-71.
[10] Sinton RA, Cuevas A. Contactless determination of current-voltage characteristics and minority-carrier lifetimes in semiconductors from quasi-steady-state photoconductance data. Appl Phys Lett 1996;69:2510-12.
[11] Miller JD, Veeramasuneni S, Drelich J, Yalamanchili MR, Yamauchi G. Effect of roughness as determined by atomic force microscopy on the wetting properties of PTFE thin films. Polym Eng Sci 1996;36:1849-55.
[12] Skorka D, Brinkmann N, Gorgulla A, Hahn G, Terheiden B. Changes in passivation quality of PECVD-deposited hydrogenated amorphous silicon layers used in solar cells due to sputter deposition of TCOs. In: Proc 28th EU PVSEC, Paris 2013. p 1162-65.